Stable and efficient seawater splitting on a porous phosphate-intercalated NiFe (oxy)hydroxide@NiMoO₄ core-shell micropillar electrode

Chen Yang¹,², Nannan Gao¹,³, Xilong Wang¹, Jiajia Lu¹, Lijuan Cao¹,³, Yadong Li¹,², Han-Pu Liang¹,²,⁴

¹Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, Shandong, China.
²Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.
³Sino-danish college, University of Chinese Academy of Sciences, Beijing 101408, China.
⁴Dalian National Laboratory for Clean Energy, Dalian 116023, Liaoning, China.

#Authors contributed equally.

Correspondence to: Prof. Han-Pu Liang, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, No. 189 Songling Road, Qingdao 266101, Shandong, China. E-mail: lianghp@qibebt.ac.cn


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Abstract

Seawater splitting powered by solar or wind sources is a significant renewable energy storage technology for the production of green hydrogen energy. However, both the chlorine evolution reaction and chloride corrosion are intractable issues in seawater splitting. Here, a porous electrode based on a phosphate-intercalated NiFe (oxy)hydroxide shell coated on a nickel molybdate (NiMoO₄) micropillar core (denoted as P-NiFe@NiMoO₄) is synthesized through an electrochemical oxidation strategy. During the electrochemical oxidation process, the etching of MoO₂ promotes the reconstruction of NiFe (oxy)hydroxide and the formation of porous structures in an alkaline solution. The optimized P-NiFe@NiMoO₄ electrocatalysts afford a low overpotential of 258 mV at a current density of 100 mA/cm² in alkaline seawater. By pairing the anode with a cathode of as-synthesized P-NiMoO₄, the electrolyzer presents a low voltage of 1.63 V at 100 mA/cm² in alkaline seawater with excellent stability. Moreover, the remarkable stability of the anode seems to be attributed to the in-situ phosphate formed during the electrochemical oxidation process to passivate chloride corrosion.
Keywords: NiFe (oxy)hydroxide, NiMoO$_4$ micropillars, oxygen evolution reaction, seawater splitting

INTRODUCTION

With the depletion of energy resources and environmental destruction, the exploration of new energy sources has become an urgent priority$^{[1-3]}$. Hydrogen is the optimal clean energy as a result of its high gravimetric energy density (142 MJ/kg) and pollution-free application$^{[4-8]}$. Although water splitting is an efficient approach to yield hydrogen, the oxygen evolution reaction (OER) represents a bottleneck owing to its sluggish four-electron process$^{[9-14]}$. Recently, considering the shortage of freshwater, there has been a dramatic increase in interest in seawater splitting because seawater is the most abundant resource globally. Nevertheless, several challenges remain before this technology can become competitive.

Excess chloride anions represent a crucial challenge during seawater splitting and they may occur in the competitive chlorine evolution reaction at the anode$^{[15,16]}$. In an alkaline solution, the chlorine furthers react with OH$^-$ to form ClO$^-$ with an onset potential that is ~490 mV higher than that of the OER. Hence, the promising overpotential of OER electrocatalysts under high current must be kept well below 490 mV, under which a seawater electrolysis efficiency of 100% can be achieved. Furthermore, the corrosion of catalysts and substrates from aggressive chloride anions in seawater is another challenge and can lead to poor long-term stability$^{[17]}$. To slow down this corrosion process, it is vital to develop corrosion-resistant electrodes for seawater splitting.

Traditionally, Pt-, Ir- and Ru-based noble metal catalysts are used for water splitting because of their relatively good activity for both the hydrogen evolution reaction (HER) and OER$^{[18-21]}$. Nevertheless, considering the high cost, scarcity and poor stability of noble metal catalysts, earth-abundant catalysts, such as transition-metal oxides$^{[22,23]}$, (oxy)hydroxides$^{[24-26]}$, phosphides$^{[27-29]}$, nitrides$^{[30,31]}$, borides$^{[32]}$, sulfides$^{[33,34]}$ and selenides$^{[35,36]}$, have been used as promising alternatives in recent years. In particular, transition-metal (oxy)hydroxides have attracted considerable attention for seawater electrolysis due to their high activity. For example, a NiFe layered double hydroxide catalyst synthesized by Dionigi $et al.$$^{[37]}$ showed a high overpotential of 359 mV at 10 mA/cm$^2$ in a simulated seawater electrolyte. More recently, Kuang $et al.$$^{[17]}$ reported that an anode based on a NiFe hydroxide-coated NiS$_2$ layer could achieve a high current density of 400 mA/cm$^2$ at an overpotential of 510 mV, which tremendously boosted the development of hydrogen production. Liu $et al.$$^{[38]}$ recently constructed a Fe-doped NiOOH catalyst by self-reconstruction, which exhibited an overpotential of 292 mV at 100 mA/cm$^2$ and excellent stability. Furthermore, the construction of highly efficient seawater splitting electrocatalysts is essential for balancing catalytic activity and stability.

Herein, we report a porous electrode based on a phosphate-intercalated NiFe (oxy)hydroxide shell coated on a nickel molybdate (NiMoO$_4$) micropillar core (denoted as P-NiFe@NiMoO$_4$) on nickel foam (NF) by an electrochemical oxidation strategy for alkaline seawater splitting. The P-NiFe@NiMoO$_4$ core-shell electrode requires low overpotentials of 238 and 258 mV at a current density of 100 mA/cm$^2$ in 1 M KOH and 1 M KOH + seawater electrolytes, respectively. Moreover, the overall alkaline seawater splitting electrolyzer, in which P-NiFe@NiMoO$_4$ is coupled with another efficient HER electrode of P-NiMoO, requires a low voltage of 1.63 V at a current density of 100 mA/cm$^2$, benefiting from the distinct porosity and large surface area. Along with excellent catalytic performance, the two-electrode electrolyzer also shows superior stability with a slight decrease over 200 h in alkaline seawater at ambient temperature, attributed to the formation of phosphate that intercalates into NiFe (oxy)hydroxide during the reconstruction process to prevent Cl$^-$ corrosion.
EXPERIMENTAL

Reagents
FeSO$_4$$ \cdot $9H$_2$O [analytical reagent (AR)], (NH$_4$)$_6$Mo$_7$O$_{24}$$ \cdot $4H$_2$O (AR), Ni(NO$_3$)$_2$$ \cdot $6H$_2$O (AR), NaH$_2$PO$_4$ (AR), KOH (AR), HCl (AR), ethanol (AR) and commercial RuO$_2$ were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd, China. With a thickness of 1.6 mm and a porosity of ~95%, NF was provided by Suzhou Jiashide Metal Foam Co., Ltd. Deionized (DI) water was obtained from a Millipore Milli-Q purification system.

Preparation of catalysts

**Synthesis of FeNiMoO and NiMoO precursors on nickel foam**
A piece of NF (2 × 4 cm$^2$) was cleaned by ultrasonication with 2 M HCl for 15 min and the substrate was then washed with ethanol and DI water several times. A mixture of 378.3 mg of Ni(NO$_3$)$_2$$ \cdot $6H$_2$O, 202 mg of FeSO$_4$$ \cdot $7H$_2$O and 395.5 mg of (NH$_4$)$_6$Mo$_7$O$_{24}$$ \cdot $4H$_2$O was dissolved in 40 mL of DI water to form a homogeneous solution. The solution and as-prepared NF substrate were then transferred to a 100 mL Teflon-lined stainless-steel autoclave, which was heated at 150 °C for 6 h. After cooling to room temperature naturally, the sample was washed with DI water several times. The NiMoO precursor was prepared similarly without the addition of FeSO$_4$$ \cdot $9H$_2$O.

**Synthesis of P-FeNiMoO, P-NiMoO and A-FeNiMoO electrodes**
A total of 400 mg of NaH$_2$PO$_4$ on porcelain was put upstream of a furnace and the as-prepared FeNiMoO precursor was put downstream. The furnace was heated at 450 °C for 2 h under an N$_2$ atmosphere. Similarly, the P-NiMoO electrode was synthesized by replacing the FeNiMoO precursor with a NiMoO precursor. The A-FeNiMoO electrode was synthesized by directly annealing the FeNiMoO precursor in a tube furnace. The annealing treatment was conducted at 450 °C for 2 h under an N$_2$ atmosphere.

**Synthesis of P-NiFe@NiMoO$_4$, A-NiFe@NiMoO$_4$ and P-Ni@NiMoO$_4$ electrodes**
An electrochemical oxidation process was deployed to synthesize the three electrodes. The P-FeNiMoO, P-NiMoO and A-FeNiMoO electrodes were electroxidized under a current density of 100 mA/cm$^2$ for 6 h to obtain P-NiFe@NiMoO$_4$, P-Ni@NiMoO$_4$ and A-NiFe@NiMoO$_4$, respectively.

**Preparation of RuO$_2$ and Pt/C catalysts on carbon paper**
To prepare the RuO$_2$ electrode for comparison, 3 mg of RuO$_2$ and 10 μL of Nafion were dispersed in 990 μL of ethanol and the mixture was ultrasonicated for 30 min. A 100 μL dispersion was then coated onto a clean carbon paper substrate, where the mass loading was 300 μg/cm$^2$, followed by drying in air. Pt/C electrodes were obtained by a similar method but with a mass loading of 30 mg/cm$^2$.

Characterization of catalysts

Physical characterization
Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy were performed with a Hitachi S-4800 scanning electron microscope equipped with an energy dispersive X-ray analyzer (HORIBA, 7593-H). Both transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed with a FEI Tecnai T20 microscope. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Advanced diffractometer using a Cu-Kα radiation source in the 2θ range of 10-80°. X-ray photoelectron spectroscopy (XPS) was performed on a K-Alpha X-ray photoelectron spectrometer (Thermo Scientific). Raman spectroscopy was recorded at ambient temperature on a DXR Raman microscope with a 532 nm excitation length.
**Electrochemical measurements**

The electrochemical performance was tested using an electrochemical workstation (CH Instruments 660E). The two half reactions of the OER and HER were each carried out at ambient temperature (25 °C) in a standard three-electrode system, with the as-prepared electrode, a graphite rod (for the HER) or Pt mesh (for the OER) and a standard Hg/HgO electrode used as the working, counter and reference electrodes, respectively. All the electrode sizes were ~1 cm$^2$ and the potentials were calibrated to the reversible hydrogen electrode with 85% iR compensation if not specified.

OER polarization curve measurements were performed by cyclic voltammetry (CV) at a scan rate of 5 mV/s and stability tests were carried out under 100 mA cm$^{-2}$ in 1 M KOH. The HER polarization curve was collected by linear sweep voltammetry at a scan rate of 5 mV/s and stability tests were carried out under 100 mA cm$^{-2}$ in 1 M KOH. Electrochemical impedance spectroscopy was measured at an overpotential of 270 mV from 0.1 Hz to 100 kHz with an amplitude of 10 mV. $C_{dl}$ was measured by CV in the non-faradaic region.

The two-electrode electrolyzer was constructed by pairing the as-prepared P-NiFe@NiMoO$_4$ with the P-NiMoO electrode as the anode and cathode, respectively. The workstation was used to measure the polarization curves in different electrolytes. The stability test was carried out with a LANHE battery tester working at a constant current density of 100 mA cm$^{-2}$ at 25 °C.

**RESULTS AND DISCUSSION**

Scheme 1 presents a schematic for the synthesis process of the porous P-NiFe@NiMoO$_4$ core-shell electrode, with NF used as the substrate benefiting from its natural conductivity, high surface area and abundant reserves. Firstly, a hydrothermal method was deployed to synthesize the FeNiMoO precursor. Secondly, the FeNiMoO precursor was put into a tube furnace for phosphorization treatment, followed by an electrochemical oxidation process. As shown in Supplementary Figure 1, the as-synthesized FeNiMoO precursor electrode turned from brown to black after the phosphorization process. It should be noted that the precursor turned from brown to dark yellow after an annealing treatment under N$_2$ atmosphere rather than phosphorization. The FeNiMoO precursor was characterized by SEM. In Supplementary Figure 2, it can be seen that the micropillars with smooth surfaces grew well on the NF. After the phosphorization process, shown in Supplementary Figure 3, the smooth surface of the P-FeNiMoO electrode was covered by a shell of dense material. In a control experiment, another electrode was synthesized with a similar procedure but heated at high temperatures without NaH$_2$PO$_2$ (denoted as A-FeNiMoO). In contrast, the A-FeNiMoO electrode in Supplementary Figure 4 shows that these micropillars were broken with cracks on the surface, possibly due to the absence of the covering dense material.

To further investigate the dense shell, a SEM image of a cross section of P-FeNiMoO is provided in Figure 1A, which clearly shows that the micropillar presents a core-shell structure. The XRD pattern of P-FeNiMoO is shown in Supplementary Figure 5. It is evident that the diffraction peaks at 26.1°, 36.7° and 53.3° could be indexed to the (110), (−211) and (220) planes of MoO$_2$ according to the Joint Committee on Powder Diffraction Standards (JCPDS) No. 78-1072 and the diffraction peaks at 14.2°, 25.3°, 28.7°, 32.5° and 47.5° could be assigned to NiMoO$_4$ according to JCPDS No. 86-0361, which indicates the presence of both NiMoO$_4$ and MoO$_2$. The XRD pattern of A-FeNiMoO was also collected and is shown in Supplementary Figure 5, where the strong peaks could be assigned to NiMoO$_4$. Moreover, a smaller amount of MoO$_2$ was obtained during the annealing treatment under N$_2$ compared with the phosphorization process. Therefore, it is envisaged that the MoO$_2$ is mainly produced from the reaction of PH$_3$ produced from the decomposition of NaH$_2$PO$_2$ with the FeNiMoO precursor in the process of phosphorization, resulting in the
formation of the core-shell micropillar structure, as shown in Figure 1A. The core corresponds to NiMoO₄ and the shell could be tentatively assigned to a hybrid containing MoO₂ and NiFe phosphorous oxide. Figure 1B and Supplementary Figure 6 show the SEM images of the P-NiFe@NiMoO₄ electrode at different magnifications, where it is clear that the surface of the micropillars became porous after the electrochemical oxidation process. The numerous pores offer large surface areas, active sites, efficient electrolyte diffusion and oxygen evolution channels. The A-FeNiMoO was electrochemically oxidized using exactly the same process as P-NiFe@NiMoO₄ (denoted as A-NiFe@NiMoO₄). The SEM images in Supplementary Figure 7 show that there is no apparent porous structure on the surface of A-NiFe@NiMoO₄, which further confirms that the formation of the porous structure is closely connected with the etching of MoO₂. The XRD pattern of P-NiFe@NiMoO₄ in Supplementary Figure 5 shows the absence of diffraction peaks associated with MoO₂ after the electrochemical oxidation process in comparison with that of P-FeNiMoO. It has been
reported that low-valence MoO$_2$ can be oxidized to high-valence MoO$_3$, which could then be dissolved in an alkaline solution owing to the instability of MoO$_3$.[39,40] Thus, the emergence of pores could be attributed to the etching of MoO$_2$, which boosts the reconstruction of the shell during electrochemical oxidation,[41] leading to the formation of the porous phosphate-intercalated NiFe (oxy)hydroxide shell.

To gain insights into the electrochemical oxidation process, *in-situ* Raman spectroscopy, as shown in Supplementary Figure 8, was conducted to investigate the surface reconstruction of the catalytic electrode with controlled potentials. For the pristine P-NiFe@NiMoO$_4$ without any potential, the Raman bands at 704, 905 and 950 cm$^{-1}$ can be assigned to the Mo-O vibrations in the MoO$_4^{2-}$ anions, while the bands at 196 and 344 cm$^{-1}$ are assigned to the Mo-O vibrations in MoO$_2$.[42] The Raman bands are stable and show a minor change when the potential is increased to 1.6 V. With the applied potential increased to 1.8 V, the MoO$_2$ bands disappear while the NiFe (oxy)hydroxide bands appear at 465 and 545 cm$^{-1}$, indicating the formation of NiFe (oxy)hydroxide under anodic potentials. The inner NiMoO$_4$ remained stable even when the potential was increased to 2.2 V, in agreement with the literature[41]. It is evidenced that the surface reconstruction contributes to the porous structure.

Figure 1C and D and Supplementary Figure 9 show the TEM images. It is clear from the TEM image in Figure 1C that a hollow structure at the lower end of the micropillar, indicated by the orange ellipse, could be tentatively attributed to the fact that the significantly greater amount of PH$_3$ gas produced during the decomposition of NaH$_2$PO$_2$ could react with the FeNiMoO precursor to generate a large amount of MoO$_2$, the etching of which leads to the formation of the hollow structure instead of pores. The HRTEM image in Figure 1E reveals that the lattice distance of 0.233 nm could be attributed to the (002) plane of Ni(OH)$_2$. The elemental mapping images and composition analysis of P-NiFe@NiMoO$_4$ from energy-dispersive X-ray spectroscopy in Figure 1F and Supplementary Figure 10, respectively, confirm that the Fe, Ni, Mo, O and P elements are uniformly distributed.

The XPS surveys of the P-NiFe@NiMoO$_4$ and P-FeNiMoO electrodes are shown in Figure 2A and Supplementary Figure 11, respectively, which further validate the existence of the Fe, Ni, Mo, O and P elements. Their contents are summarized in Supplementary Table 1. The decrease in Mo content from 7.23% to 0.36% proves the etching of MoO$_2$ during the electrochemical oxidation process. It can be seen in Figure 2B that the two peaks located at 712.2 and 724.3 eV are assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ levels of Fe(III), respectively, indicating the presence of the Fe$^{3+}$ oxidation state.[43] The peak at 705.2 eV is assigned to Ni Auger electrons.

The high-resolution X-ray photoelectron spectrum of Ni 2p in Figure 2C demonstrates not only that the peaks located at 872.9 and 855.2 eV are from Ni(OH)$_2$ with a binding energy gap of 17.7 eV[44,45] but also that the peaks located at 875.5 and 856.9 eV from NiMoO$_4$ are observed.[46] In addition, the spectrum of Mo 3d in Figure 2D shows that the two peaks at 235.6 and 232.4 eV belong to Mo$^{2+}$, thereby further confirming the presence of the inside core of NiMoO$_4$ after the electrochemical oxidation process based on the presence of Ni$^{2+}$ in Figure 2C.[47]. The low valence of Mo is shown in Supplementary Figure 12A, which is consistent with the above TEM image and XRD results. As for the O 1s spectrum [Figure 2E], the three peaks at 532.9, 530.9 and 528.9 eV are assigned to H-O-H, metal-OH and metal-O, respectively.[48] The strong P-O peak at 134.3 eV in the P 2p spectrum [Figure 2F] is assigned to the presence of phosphate[49]. Nevertheless, the P-O peak at 133.5 eV in Supplementary Figure 12B negatively shifts, which indeed confirms the formation of NiFe phosphorous oxide after phosphorization. In summary, a porous phosphate-intercalated NiFe (oxy)hydroxide shell covered on NiMoO$_4$, which consists of Ni(OH)$_2$, and FeOOH, appears to have been
Figure 2. (A) X-ray photoelectron spectroscopy survey and high-resolution spectra of (B) Fe 2p, (C) Ni 2p, (D) Mo 3d, (E) O 1s and (F) P 2p for P-NiFe@NiMoO₄ electrode.

formed through a surface reconstruction during the electrochemical oxidation process under high potentials.

To evaluate the OER performance of the P-NiFe@NiMoO₄ catalysts, a three-electrode system was deployed in 1 M KOH. A-NiFe@NiMoO₄, P-Ni@NiMoO₄ and commercial RuO₂ were also used as benchmarks for comparison. From the polarization curves shown in Figure 3A and Supplementary Figure 13, it can be seen that the P-NiFe@NiMoO₄ electrode exhibits a significant improvement for the OER, compared with A-NiFe@NiMoO₄ and P-Ni@NiMoO₄ and commercial RuO₂. Figure 3B delivers current densities of 100 and 200 mA/cm² at small overpotentials of 238 and 257 mV in 1 M KOH, respectively. In addition, even at a higher current density of 300 mA/cm², the required overpotential is 266 mV. The overpotential of the P-NiFe@NiMoO₄ electrode is well below that of the other as-synthesized electrodes, such as A-NiFe@NiMoO₄ and P-Ni@NiMoO₄, despite the different current densities. The above results further confirm that the
introduction of Fe and P plays a vital part in enhancing the OER performance. Notably, the P element is oxidized to phosphate, which intercalates into the NiFe (oxy)hydroxide layer to resist corrosion from Cl⁻.

The Tafel plot in Figure 3C shows that the P-NiFe@NiMoO₄ electrode exhibits a smaller Tafel slope (54.3 mV/dec) compared with A-NiFe@NiMoO₄ (83.1 mV/dec) and P-Ni@NiMoO₄ (81.8 mV/dec), suggesting its rapid electrocatalytic kinetics. The high electrochemically active surface area is positively related to the number of active sites, which is calculated from the double-layer capacitance ($C_{dl}$). Figure 3D
presents the $C_{dl}$ values from the CV curves [Supplementary Figure 14]. The $C_{dl}$ values of the P-NiFe@NiMoO$_4$, A-NiFe@NiMoO$_4$ and P-Ni@NiMoO$_4$ electrodes are 9.2, 6.8 and 5.1 mF/cm$^2$, respectively, implying the highly enhanced surface area and growing active sites implemented by forming the porous NiFe (oxy)hydroxide shell coated on the NiMoO$_4$ micropillars. Electrochemical impedance spectroscopy [Supplementary Figure 15] shows that the charge-transfer resistance ($R_{ct}$) of the P-NiFe@NiMoO$_4$ electrode is minor (0.11 $\Omega$) compared with A-NiFe@NiMoO$_4$ (0.19 $\Omega$) and P-Ni@NiMoO$_4$ (0.51 $\Omega$), thereby validating its outstanding electronic conductivity and charge transfer. Therefore, the improved OER activity benefits from the large surface area and efficient charge transfer of the porous shell on the NiMoO$_4$ micropillars. Stability is another important parameter that is assessed by chronopotentiometric measurements of the P-NiFe@NiMoO$_4$ electrode at a current density of 100 mA/cm$^2$ in 1 M KOH at 25 °C. The chronopotentiometric curve of the P-NiFe@NiMoO$_4$ electrode at a current density of 100 mA cm$^{-2}$ in 1 M KOH in Figure 3E indicates that the electrochemical catalytic activity remains constant over 100 h without a noticeable decrease.

An efficient HER catalyst based on the P-NiMoO electrode [Supplementary Figures 16 and 17] was also successfully synthesized to combine with the P-NiFe@NiMoO$_4$ electrode for overall seawater splitting. The HER performance of the P-NiMoO, P-FeNiMoO and A-NiMoO electrodes and commercial Pt/C were tested in 1 M KOH. Supplementary Figure 18A shows that the P-NiMoO electrode could deliver similar overpotentials to the P-FeNiMoO electrode below a current density of 50 mA/cm$^2$ while exhibiting superior performance above 50 mA/cm$^2$. The overpotential of the P-NiMoO electrode is only 149 mV at a current density of 100 mA/cm$^2$, which is higher than that of the A-NiMoO and P-FeNiMoO electrodes. Supplementary Figure 18B and C show that the P-NiMoO electrode presents a smaller Tafel slope of 53 mV/dec and $R_{ct}$ of 0.7 $\Omega$. The $C_{dl}$ value [Supplementary Figure 18D] of the P-NiMoO electrode is 1.076 mF/cm$^2$, calculated from the CV plots [Supplementary Figure 19]. Moreover, the stability test was carried out in 1 M KOH at a current density of 100 mA/cm$^2$ and the result demonstrates no significant decrease over 100 h [Supplementary Figure 20].

The OER and HER activities of the P-NiFe@NiMoO$_4$ and P-NiMoO electrodes were then evaluated in simulated seawater (1 M KOH + 0.5 M NaCl) and alkaline seawater (1 M KOH + seawater). The polarization curves in Figure 4A show that the P-NiFe@NiMoO$_4$ electrode retains superior OER activity in 1 M KOH + 0.5 M NaCl, requiring overpotentials of 258, 290 and 312 mV to achieve 100, 200 and 300 mA/cm$^2$, respectively [Figure 4B]. Moreover, in 1 M KOH + seawater, the activity decreases slightly owing to some insoluble precipitate$^{[16,28]}$. Even in this situation, the overpotentials of the P-NiFe@NiMoO$_4$ electrode, at current densities of 100, 200 and 300 mA/cm$^2$, are still 258, 291 and 317 mV, respectively, which surpass those of most reported catalysts [Supplementary Table 2]. Furthermore, the HER activity of the P-NiMoO electrode was also tested in 1 M KOH + 0.5 M NaCl and 1 M KOH + seawater, which requires a similar overpotential of 146 mV at a current density of 100 mA/cm$^2$ [Supplementary Figure 21].

A two-electrode electrolyzer was set up to further investigate the overall seawater splitting performance in different electrolytes [Figure 4C], where the P-NiFe@NiMoO$_4$ electrode (anode) was coupled with the P-NiMoO electrode (cathode). Remarkably, this electrolyzer exhibits outstanding performance with a low cell voltage of ~1.63 V under a current density of 100 mA/cm$^2$ in both the 1 M KOH + 0.5 M NaCl and 1 M KOH + seawater electrolytes. Even at larger current densities, the performance is still impressive, outperforming most previously reported electrolyzers [Supplementary Table 3]. The Faradaic efficiency was then evaluated in 1 M KOH + seawater by collecting the evolved H$_2$ and O$_2$ gases [Supplementary Figure 22]. As shown in Figure 4D, the molar ratio of H$_2$ to O$_2$ approaches 2:1 and the measured gas volume is in good agreement with the calculated volume, presenting high Faradaic efficiency.
Figure 4. (A) Polarization curves and (B) comparison of overpotentials at different current densities of 100, 200 and 300 mA cm$^{-2}$ of P-NiFe@NiMoO$_4$ electrode tested in different electrolytes. (C) Overall seawater spilling polarization curves in different electrolytes. Inset illustrates the overall two-electrode seawater splitting electrolyzer that paired P-NiFe@NiMoO$_4$ with P-NiMoO. (D) Comparison between the amount of collected and theoretical gaseous products (H$_2$ and O$_2$) by the two-electrode electrolyzer at a constant current density of 40 mA cm$^{-2}$ in 1 M KOH + seawater at 25 °C. (E) Durability tests of electrolyzer at a constant current density of 100 mA cm$^{-2}$ in 1 M KOH + seawater at 25 °C. (F) Raman spectra of P-NiFe@NiMoO$_4$. 

and selectivity. Moreover, the as-synthesized P-NiFe@NiMoO$_4$||P-NiMoO electrolyzer presents excellent stability over 200 h in 1 M KOH + seawater [Figure 4E], while the stability of the A-NiFe@NiMoO$_4$||P-NiMoO electrolyzer decreases dramatically, indicating the promotion of stability in the presence of phosphate.

For further clarification of phosphate in the P-NiFe@NiMoO$_4$ electrode, Raman spectroscopy [Figure 4F] was conducted, notably showing the presence of phosphate with peaks at 409.8, 588.2 and 948.8 cm$^{-1}$.
assigned to P-O vibrations. The other two strong peaks, at 465.7 and 540.9 cm\(^{-1}\), are assigned to NiFe (oxy)hydroxide. Peaks of MoO\(_4^{2-}\) located at 706.8, 907.4 and 960.4 cm\(^{-1}\) can also be observed, which is consistent with the XRD result, confirming the NiMoO\(_4\) micropillars anchored on the NF substrate.

The morphology of the P-NiFe@NiMoO\(_4\) electrode after seawater splitting was investigated by SEM [Supplementary Figure 23]. After 200 h of electrolysis, the NiMoO\(_4\) micropillars still maintain their initial structure of being firmly anchored on the NF. On the surface of the NiMoO\(_4\) micropillars, nanoarrays were formed due to the reconstruction of the Ni and Fe elements during long-term stability under a high potential. Overall, the P-NiFe@NiMoO\(_4\) || P-NiMoO electrolyzer works well and delivers a superior cell voltage, indicating its potential application in hydrogen production.

CONCLUSIONS

In summary, we have successfully demonstrated the use of a porous anode made up of phosphate-intercalated NiFe (oxy)hydroxide@NiMoO\(_4\) core-shell micropillars for active and stable seawater splitting. The introduction of Fe and the phosphorization are incredibly beneficial to the enhancement of activity and stability. During electrochemical oxidation, the etching of MoO\(_2\) results in a reconstruction process on the micropillars’ surface, which generates a porous phosphate-intercalated NiFe (oxy)hydroxide shell. The large pores endow the P-NiFe@NiMoO\(_4\) electrode with a large surface area, numerous active sites and efficient charge transfer. The P-NiFe@NiMoO\(_4\) electrode exhibits a low overpotential of 258 mV at a current density of 100 mA/cm\(^2\) in alkaline seawater. In addition, by pairing the anode with a P-NiMoO cathode, the two-electrode electrolyzer outputs a current density of 100 mA/cm\(^2\) at a low voltage of 1.63 V. The electrolyzer also exhibits superior stability over 200 h without any apparent activity loss, which is attributed to the passivating anions of phosphate against chloride corrosion. This work provides insight into the development of the industrial application of seawater splitting for green hydrogen production.

DECLARATIONS

Authors’ contributions
Methodology, investigation, formal analysis, writing manuscript, visualization: Yang C, Gao N
Validation, resources, formal analysis: Wang X
Validation, investigation: Lu J, Li Y
Formal analysis, validation: Cao L
Project administration, conceptualization, funding acquisition, supervision, writing manuscript: Liang HP

Availability of data and materials
The data supporting our findings can be found in the supplementary information.

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Conflicts of interest
All authors declared that there are no conflicts of interest.
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